

O 105: Nanostructures at surfaces: 1D and 2D structures and networks III

Time: Thursday 17:15–18:15

Location: MA 141

O 105.1 Thu 17:15 MA 141

Electrochemical switching of π -expanded macrocycles observed by STM/STS — ●JOSE D. COJAL GONZALEZ¹, MASAHIKO IYODA², and JÜRGEN P. RABE¹ — ¹Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin — ²Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo

Macrocytic oligothiophenes and their π -extended derivatives have attracted attention for their potential applications in molecular electronics and as components in molecular devices [1]. Here we investigated self-assembled monolayers of four π -expanded oligothiophene macrocycles 8-mers at the interface between their octanoic acid solutions and highly oriented pyrolytic graphite (HOPG). STM height images showed hexagonal ordered 2D-networks with a small difference in unit cells. I–V characteristics confirmed the donor like character of the macrocycles, whose HOMO and LUMO position were consistent with TD-DFT calculations. Moreover, optical gaps determined from UV-Vis absorption and TD-DFT resulted in accordance with the effective gap measured by STS. Cyclic STS measurements showed the switching from the diastereomer *Z,Z*-8-mer to the *E,E*-8-mer form after formation of a most stable cationic species, which confirms voltammetry and chemical oxidation experiments. To the best of our knowledge, this result represents the first electrochemical switching experiment under standard STM conditions.

[1] M. Iyoda and H. Shimizu. *Chem. Soc. Rev.*, **44**(18): 6411-6424, 2015

O 105.2 Thu 17:30 MA 141

Crossover in the inelastic spectra of highly-conducting conjugated molecules — ●ENRIQUE MONTES, GIUSEPPE FOTI, and HÉCTOR VÁZQUEZ — Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, Prague, Czech Republic

We use inelastic electron tunnelling spectroscopy (IETS) first-principles simulations [1] to identify and characterise the different vibrational modes of single conjugated molecules bonded to Au metal electrodes. The molecules are polyphenyls (with 1 to 4 benzene units) bonded to Au via highly conducting direct Au-C bonds. The short molecule shows near resonant elastic transmission, with a crossover to tunnelling for the longer backbones [2].

The calculated inelastic spectra exhibit dips for the short molecule, and peaks for the longer molecules, in the second derivative of the current. We first characterize the inelastic spectra in terms of IETS selection rules [3]. We then analyze the observed trends as a function of molecular length. In particular, we characterize the modes whose inelastic signal increases with the number of phenyl units, the modes where it decreases, and the modes where IETS dips change to peaks.

[1] T. Frederiksen, M. Paulsson, M. Brandbyge, and A.-P. Jauho. *Phys. Rev. B* **75**, 205413 (2007).

[2] W. Chen, J. R. Widawsky, H. Vázquez, S. T. Schneebeli, M. S. Hybertsen, R. Breslow, and L. Venkataraman. *J. Am. Chem. Soc.* **133**, 17160 (2011).

[3] M. Paulsson, T. Frederiksen, H. Ueba, N. Lorente, and M. Brandbyge. *Phys. Rev. Lett.* **100**, 226604 (2008).

O 105.3 Thu 17:45 MA 141

Hierarchical nanostructures by combining block copolymer and nanosphere lithography — ●DANIEL KOOL^{1,2}, KATHARINA BRASSAT^{1,2}, and JÖRG K. N. LINDNER^{1,2} — ¹Paderborn University, Dept. of Physics, Paderborn, Germany — ²Center for Optoelectronics and Photonics Paderborn (CeOPP), Paderborn, Germany

Block copolymer (BCP) lithography is a well-established technique for economical large-area surface structuring exploiting the microphase separation of a copolymer, here poly(styrene-*b*-methylmethacrylat) (PS-*b*-PMMA) BCP into self-assembled nanopatterns. Using a block length ratio of 70:30 we achieve perpendicular, 17 nm diameter PMMA cylinders hexagonally arranged in a PS-Matrix. After removing selectively the PMMA cylinders a pore density up to $9.5 \cdot 10^{10} \text{ cm}^{-2}$ is achieved. SEM images are evaluated by a self-written Delaunay-triangulation based software. In order to guide the self-assembly process of nanopores, we prepattern the substrate surface using nanosphere lithography (NSL). To this end convective self-assembly of polystyrene nanospheres in a colloidal suspension is used to generate a hexagonally close packed array of spheres. Spheres are shrunk in an oxygen plasma and used as a shadow mask in a metal thin film deposition. After removal of the sphere mask a hexagonal array of open cylinders (antidots) in the metal film is achieved. We demonstrate that using these antidots as template for the BCP lithography allows for the site-selective creation of both nanopore arrays and concentric PS rings inside antidots.

O 105.4 Thu 18:00 MA 141

Antiaromaticity as p-doping of the aromatic electronic structure. — ●NARENDRA PRABHAKAR ARASU and HÉCTOR VÁZQUEZ — Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10/112, Prague, Czech Republic

Hückel's rule states that cyclic and planar π -system is aromatic when it shares $4n + 2 \pi$ -electrons and antiaromatic when it possesses $4n$ electrons. Electrochemical studies had predicted antiaromatic molecules to have excellent conducting properties [1,2] but their instability limited their study. Recently, the single molecule conductance of a genuinely antiaromatic molecule was measured for the first time [3].

In this talk, I will describe our study on the electronic structure and conductance of aromatic and antiaromatic molecular junctions using first-principle calculations. First, I will compare the conductance of an aromatic porphyrin backbone with that of a norcorrole antiaromatic unit. We found that the conductance of the antiaromatic molecule was much higher than that of the aromatic counterpart [3]. I will then generalize this analysis to a series of aromatic-antiaromatic pairs of molecules. From a quantitative analysis of the similarity in their electronic structure, antiaromaticity is found to correspond to p-doping of the aromatic electronic structure. We generalize this analysis to explain the higher conductance of quinones [2] and discuss the implications for single molecule transport.

[1] R. Breslow et al., *J. Am. Chem. Soc.*, **95** (20), 6688 (1973). [2] R. Breslow et al., *J. Phys.: Condens. Matter*, **20**, 374104 (2008). [3] S. Fujii et al., *Nat. Commun.*, **8**, 15984 (2017).